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RESIN COMPOSITION WITH EXCELLENT ANTISTATIC PROPERTIES

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Claims

1. Resin composition with excellent antistatic properties, obtained by mixing 1-60 wt% of (A) a polyalkylene oxide or its derivative having at least one functional group that is reactive with molecular carboxy groups and 99-40 wt% of (B) a modified vinyl polymer containing carboxy groups.

Detailed explanation of the invention

The present invention concerns antistatic resin compositions having permanent antistatic properties.

Synthetic polymer materials are used in a wide range of areas for their excellent characteristics. However, in general, they have a high electrical resistance and are statically charged easily, thus various problems caused by static electricity may occur. Antistatic properties may be imparted to synthetic polymer materials by (1) compounding polymers with antistatic agents and water-absorbent compounds such as polyalkylene oxides or (2) coating surfactants on the polymer surface. However, sufficient antistatic properties are not realized, and such antistatic properties may be eliminated by washing with water or the compounded components may bleed out to the surface, adversely affecting the product qualities.

On the other hand, it has been proposed that antistatic polymers be prepared by copolymerizing vinyl monomers with hydrophilic monomers such as methoxypolyethylene glycol acrylate, N-vinylpyrrolidone, etc. (e.g., Japanese Kokai Patent Application No. Sho 50[1975]-78642). However, due to moisture absorption, such resins have low mechanical properties as molding resins, and the high cost of the hydrophilic monomers may drive up the resin cost. Thus. they are not satisfactory either.

As a result of an intense investigation for the purpose of developing high-performance antistatic resins having permanent antistatic properties, we have discovered that antistatic resin compositions satisfying such purposes can be obtained by blending certain polyalkylene oxides or derivatives with carboxy group-containing modified vinyl polymers. Thus, the present invention is attained.

Namely, the present invention is to provide resin composition with excellent antistatic properties, obtained by mixing 1-60 wt% of (A) a polyalkylene oxide or its derivative having at

least one functional group reactive with molecular carboxy groups and 40-99 wt% of (B) a modified vinyl polymer containing carboxy group.

In the resin compositions of the present invention, reactive functional groups such as hydroxy groups, etc. in the polyalkylene oxide or its derivatives form chemical bonds with the carboxy groups in the modified vinyl compounds during the mixing, resulting in excellent miscibility of the two and high antistatic effects.

The polyalkylene oxides or their derivatives (A) that can be used in the present invention have a structural unit represented by the formula (I) shown below and are polymeric compounds having at least one functional group in the molecule that can react with carboxy groups:

$$\left(\underset{R_1}{\underset{|}{CH}} - \underset{R_2}{\underset{|}{CH}} - O \right)_n \tag{I}$$

In the formula, R_1 and R_2 represent hydrogens or alkyl groups of 1-10 carbon atoms or both. Usually, both R_1 and R_2 represent hydrogen atoms or one of R_1 and R_2 represents a hydrogen while the other represents a methyl group. The degree of polymerization n in the formula is usually, but not limited to, 4-500.

The carboxy group-reactive functional group in the polyalkylene oxide or its derivatives is usually a hydroxy group, while it may also be an epoxy group, amino group, etc. The functional group is usually located at the end of the molecular chain, while it can be at other positions. Usually, the hydroxy group is located at one or both ends of the polyalkylene oxide molecular chain, while those with a methoxy end group, ether type derivatives or ester type derivatives with organic acids such as fatty acids can also be used. While polyalkylene oxides or their derivatives with various structures can be used, it is essential that they contain at least one carboxy group-reactive functional group to realize the effects of the present invention. Specific examples of the polyalkylene oxide or its derivatives used in the present invention include polyethylene glycol and polypropylene glycol, polyethylene glycol ethers such as polyethylene glycol monooctyl ether, polyethylene glycol monododecyl ether, etc., and polyethylene glycol esters such as polyethylene glycol monolaurate, polyethylene glycol monostearate, etc. However, they are not limited to such examples.

The carboxy group-containing modified vinyl polymers (hereafter referred to as modified vinyl polymers) (B) used in the present invention have structures obtained by homopolymerization or copolymerization of one or more vinyl monomers and contain carboxy groups in the molecule. The carboxy groups may be in the form of carboxy anhydrides, and the carboxy group content may be small or large within a range that does not adversely affect the resins.

Usually, the effects of the present invention can be realized when one modified vinyl polymer molecule contains one or more carboxy groups on average. While not restricted in any particular way, methods for introducing carboxy groups to the modified vinyl polymers include (1) copolymerization of certain vinyl monomers with vinyl monomers having carboxy groups or carboxy anhydride groups, such as acrylic acid, methacrylic acid, maleic acid, maleic anhydride, phthalic acid, itaconic acid, etc.; (2) (co)polymerization of certain vinyl monomers using carboxy group-containing polymerization initiators such as γ,γ′-azobis(γ-cyanovaleric acid), α,α′-azobis(α-cyano)ethyl-p-benzoic acid, persuccinic acid, etc., and/or carboxy group-containing degree of polymerization control agents such as thioglycolic acid, α-mercaptopropionic acid, β-mercaptopropionic acid, α-mercaptoisobutyric acid, 2-, 3-, or 4-mercaptobenzoic acid, etc.; (3) alkaline saponification of (co)polymers of (meth)acrylic acid esters such as methyl methacrylate, butyl acrylate, etc.

While not restricted in any particular way, the monomers that can be used in the polymerization for modified vinyl polymers are, e.g., aromatic vinyl monomers such as styrene, α-methylstyrene, etc.; cyanovinyl monomers such as acrylonitrile, methacrylonitrile, etc.; (meth)acrylic acid ester monomers such as methyl methacrylate, butyl acrylate, etc.; α,β-unsaturated carboxylic acids (anhydrides) such as maleic acid, maleic anhydride, etc.; olefin monomers such as ethylene, propylene, etc.; vinyl monomers such as vinyl chloride, vinyl acetate, butadiene, etc. They may be used alone or as mixtures. If needed, such vinyl monomers may be used together with rubber polymers such as polybutadiene, acrylonitrile/butadiene copolymer (NBR), styrene-butadiene copolymer (SBR), polybutyl acrylate, ethylene/propylene/diene rubber (EPDM), etc. While not restricted in any particular way, the modified vinyl polymers can be prepared by conventional methods, such as bulk polymerization, solution polymerization, suspension polymerization, emulsion polymerization, bulk-suspension polymerization, etc.

The compounding ratio of the resin compositions of the present invention is preferably 1-60 wt%, preferably 5-40 wt% of polyalkylene oxide or its derivative and 40-99 wt%, preferably 60-95 wt% of modified vinyl polymer. With a content of polyalkylene oxide or its derivative of less than 1 wt%, the antistatic effect is not sufficient, while with a content greater than 60 wt%, the performance of the resin, starting with mechanical strength, suffers; these amounts are thus not favored.

While not restricted in any particular way, the resin compositions of the present invention can be prepared by conventional methods involving premixing of the polyalkylene oxide or its derivative and the modified vinyl polymer, followed by melt blending by an extruder and then pelletization. Also, both ingredients may be dissolved in a solvent such as methyl ethyl ketone,

methyl isobutyl ketone, toluene, xylene, ethylbenzene, etc., then mixed and recovered. Also, both are mixed with or without solvent, mixed with a catalyst, heated, and stirred.

The resin compositions of the present invention may be blended with thermoplastic resins such as polystyrene, polymethyl methacrylate, styrene/acrylonitrile copolymer (SAN resin), acrylonitrile/butadiene/styrene copolymer (ABS resin), methyl methacrylate/butadiene/styrene copolymer (MBS resin), etc. for improved characteristics for molding resins. It is possible to further improve the antistatic properties by adding antistatic agents such as anionic or cationic surfactants; antistatic agents, various stabilizers such as UV stabilizers, etc., pigments, dyes, lubricants, plasticizers, etc. may be added as needed.

Next, the present invention is explained in further detail with examples. The volume resistivity was measured in 3 mm-thick angular injection molded plates at 23°C and 50% RH using an SM10 insulation meter from Toa Denpa Kogyo Co. Parts are by weight.

Reference examples

Preparation of carboxy group-containing modified vinyl polymer (B)

B-1: Modified vinyl polymer (B-1) obtained by copolymerization of 70 parts of styrene, 28 parts of acrylonitrile and 2 parts of acrylic acid

B-2: Modified vinyl polymer (B-2) obtained by copolymerization of 95 parts of methyl methacrylate and 5 parts of methacrylic acid

B-3: Modified vinyl polymer (B-3) obtained by copolymerization of 90 parts of styrene and 10 parts of maleic anhydride

B-4: Modified vinyl polymer (B-4) obtained by copolymerization of a mixture of 40 parts of styrene, 45 parts of methyl methacrylate, 15 parts of acrylonitrile and 0.5 part of thioglycolic acid using 0.3 part of azobisisobutyronitrile.

B-5: Modified vinyl polymer (B-5) obtained by polymerization of 100 parts of styrene and 0.6 part of β-mercatpopropionic acid using benzoyl peroxide as the initiator.

B-6: Modified vinyl polymer (B-6) obtained by copolymerization of 70 parts of styrene, 30 parts of acrylonitrile and 0.5 part of α-mercaptopropionic acid using persuccinic acid as the initiator.

The volume resistivity of each vinyl polymer (B-1 ~ B-6) was measured.

Application examples

The modified vinyl polymers (B) prepared in the reference examples and the following polyalkylene oxides (A) were compounded at the ratios shown in Table 1.

PEG-400: polyethylene glycol with average molecular weight of 400

PEG-1000 polyethylene glycol with average molecular weight of 1000

PEG-2000 polyethylene glycol with average molecular weight of 2000
MePEG-1000 methoxypolyethylene glycol with average molecular weight of 1000

The compounds are treated by the method shown below to obtain resin compositions.

(1) The compound was melt kneaded in a vented 40 mmø extruder at a resin temperature of 190°C, extruded and pelletized (kneading method, assigned M in Table 1).

(2) A mixture of 100 parts of the compound and 100 parts of xylene (solvent) was refluxed for 5 h and freed from the solvent (reflux method, assigned R in Table 1).

The resin compositions obtained were injection-molded to 3 mm-thick angular plates, the volume resistivities of which were measured under the conditions given below.

(1) Measurement was performed after conditioning at 23°C and 50% RH for 24 h immediately following molding.

(2) Immediately after molding, the specimen was washed with an aqueous solution of the detergent Mamalemon [transliteration] (product of Lion Yushi Co.), followed by washing with distilled water, removing water from the surface, conditioning at 50% RH and 23°C for 24 h, then measurement.

(3) Specimens allowed to stand at 23°C and 50% RH for 200 days were then measured.

(4) Specimens molded in this manner were allowed to stand at 23°C and 50% RH for 200 days, washed with an aqueous solution of the detergent Mamalemon, washed with distilled water, freed from surface water, conditioned at 23°C and 50% RH for 24 h, and measured.

Measurement results are given in Table 1.

Comparative examples

Carboxy group-free vinyl polymers such as styrene/acrylonitrile = 70/30 (weight ratio) copolymer (SAN), polymethyl methacrylate (PMMA) and polystyrene (PS) were compounded with polyalkylene oxide similarly as in the application examples to obtain resin compositions. In compounding at various composition ratios, the carboxy group-free vinyl polymers showed poor miscibility with polyalkylene oxide (A). With a polyalkylene oxide (A) content above 10 wt%, the resin performance characteristics such as mechanical strength, etc. could not be maintained. The volume resistivities of the vinyl polymer itself and compositions of 90 parts of vinyl polymer and 10 parts of polyalkylene oxide (A) were measured. Results are given in Table 1.

vinyl poly

Table 1

	樹脂組成物					体積固有抵抗値 (Ω·cm)			
	ポリアルキレンオキサイド		ビニル系重合体		製造法	成形直後		200日間放置	
	名称	配合量 (部数)	名称	配合量 (部数)	混練法 (M) または還流法 (R)	(1) 熱処理	(2) 水洗	(3) 熱処理	(4) 水洗
実施例 1	PEO-400	5	B-1	95	M	6×10^{11}	7×10^{11}	4×10^{11}	7×10^{11}
2	PEO-400	30	B-1	70	R	7×10^{9}	9×10^{9}	5×10^{9}	6×10^{9}
3	PEO-1000	10	B-1	90	M	8×10^{11}	9×10^{11}	6×10^{11}	9×10^{11}
4	PEO-2000	40	B-1	60	M	1×10^{9}	1×10^{9}	5×10^{9}	7×10^{9}
5	MePEO-1000	50	B-1	50	R	4×10^{9}	4×10^{9}	6×10^{9}	4×10^{9}
6	PEO-1000	10	B-2	90	M	5×10^{11}	7×10^{11}	5×10^{11}	6×10^{11}
7	MePEO-1000	40	B-2	60	R	8×10^{9}	1×10^{9}	7×10^{9}	8×10^{9}
8	PEO-2000	10	B-3	90	M	1×10^{12}	2×10^{12}	9×10^{11}	1×10^{12}
9	MePEO-1000	50	B-3	50	R	6×10^{9}	6×10^{9}	5×10^{9}	6×10^{9}
10	PEO-400	10	B-4	10	M	7×10^{11}	8×10^{11}	7×10^{11}	9×10^{11}
11	PEO-1000	20	B-4	80	R	2×10^{10}	3×10^{11}	1×10^{10}	5×10^{11}
12	PEO-400	10	B-5	90	R	8×10^{11}	8×10^{11}	7×10^{11}	8×10^{11}
13	PEO-1000	30	B-5	70	R	8×10^{9}	9×10^{9}	7×10^{9}	9×10^{9}
14	PEO-400	10	B-6	90	M	9×10^{11}	9×10^{11}	8×10^{11}	9×10^{11}
15	MePEO-1000	30	B-6	70	R	9×10^{9}	1×10^{10}	6×10^{9}	7×10^{9}
比較例	—		B-1	100	M	4×10^{14}			
	—		B-2	100	M	5×10^{14}			
	—		B-3	100	M	5×10^{14}			
	—		B-4	100	M	4×10^{14}			
	—		B-5	100	M	8×10^{14}			
	—		B-6	100	M	4×10^{14}			
比較例	—		SAN	100	M	6×10^{14}			
	PEO-400	10	SAN	90	R	2×10^{13}	7×10^{13}	8×10^{13}	7×10^{13}
	PEO-1000	10	SAN	90	M	3×10^{13}	6×10^{13}	8×10^{13}	8×10^{13}
	PEO-2000	10	SAN	90	M	5×10^{13}	7×10^{13}	1×10^{13}	7×10^{13}
	MePEO-1000	10	SAN	90	R	7×10^{13}	9×10^{13}	2×10^{13}	9×10^{13}
	—		PMMA	100	M	3×10^{14}			
	PEO-400	10	PMMA	90	M	3×10^{13}	9×10^{13}	7×10^{13}	8×10^{13}
	MePEO-1000	10	PMMA	90	R	6×10^{13}	8×10^{13}	9×10^{13}	7×10^{13}
	—		PS	100	M	8×10^{14}			
	PEO-400	10	PS	90	R	2×10^{13}	9×10^{13}	7×10^{13}	9×10^{13}
	PEO-1000	10	PS	90	R	2×10^{13}	8×10^{13}	8×10^{13}	9×10^{13}

Key:
1 Resin composition
2 Polyalkylene oxide
3 Vinyl polymer
4 Preparation method
5 Name
6 Compounding amount (parts)
7 Kneading method (M) or reflux method (R)
8 Volume resistivity
9 Immediately after molding
10 After allowing to stand for 200 days
11 Heat treatment

12 Washing with water
13 Application examples
14 Reference examples
15 Comparative examples

The following are apparent from the results of the application examples and the comparative examples. Compounding polyalkylene oxide (A) with the usual carboxy group-free vinyl polymers does not provide sufficient antistatic properties, and the antistatic properties decrease greatly upon washing with water or with the lapse of time. On the other hand, carboxy group-containing modified vinyl polymer (B) and polyalkylene oxide (A) show good miscibility, and by compounding with polyalkylene oxide (A), high antistatic properties are obtained that do not decrease upon washing with water or the lapse of time. Namely, the resin compositions of the present invention have excellent permanent antistatic properties.